

**INORGANIC ANIONS by ION CHROMATOGRAPHY{PRIVATE }**  
 Bromide, Chloride, Fluoride, Nitrate-N, Nitrite-N, orthophosphate-P, and  
 Sulfate

EPA Method 300.0 (Revision 2.1, August 1993)

**Table 1. Summary of Contract Required Detection Limits, Holding Times, and Preservation for Inorganic Anions**

{PRIVATE }Analytical Parameter	Contract Required Detection Limit (CRDL)	Technical and Contract Holding Times	Preservation
Nitrate-N (NO <sub>3</sub> -N) Nitrite-N (NO <sub>2</sub> -N) ortho-Phosphate-P (HPO <sub>4</sub> -P)	0.10 mg/L 0.10 mg/L 1.0 mg/L	Technical: 48 hours from collection; Contract: 24 hours from receipt at laboratory	Cool to 4°C ±2°C
Bromide (Br) Chloride (Cl) Fluoride (F) Sulfate (SO <sub>4</sub> )	1.0 mg/L 1.0 mg/L 0.10 mg/L 1.0 mg/L	Technical: 28 days from collection; Contract: 25 days from receipt at laboratory	Cool to 4°C ±2°C

**Data Calculations and Reporting Units:**

Calculate the sample results according to Section 12 of EPA Method 300.0. Report sample results in concentration units of milligram per liter (mg/L) for bromide, chloride, fluoride, and sulfate. Report sample results in mg/L as nitrogen for nitrate and nitrite, and as phosphorous for orthophosphate. Report anion concentrations that are less than 10 mg/L to 2 significant figures, and anion concentrations that are greater than or equal to 10 mg/L to 3 significant figures.

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- a) If the number following those to be retained is greater than 5, round up; or
- b) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

Table 2. Summary of Calibration Procedures for Inorganic Anions by EPA Method 300.0

{PRIVATE }Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 3 points for each analyte) (ICAL) <sup>a, b</sup>	Initially; whenever required, due to failure of ICV or IPC	$r \geq 0.995$	1. Terminate analysis 2. Recalibrate and verify before sample analysis
Initial Calibration Verification (ICV) at midpoint of ICAL (Separate source from ICAL standards)	Daily, prior to sample analysis; immediately following ICAL; after 20 samples	$\pm 10\%$ from expected concentration	1. Reprep ICV and reanalyze all associated samples 2. Identify and document problem 3. Recalibrate and reanalyze reprepmed ICV and all associated samples
Instrument Performance Check (IPC)	Following ICV and before sample analysis; after every 10 samples and end of run	$\pm 10\%$ from expected concentration	1. Recalibrate and verify 2. Reanalyze samples back to last good IPC
Retention time evaluation for IPC and ICV standards	Each analysis of IPC and ICV standards	$\pm 10\%$ from expected retention times	1. Recalibrate and verify 2. Reanalyze samples back to last good IPC
Calibration Blank Verification (ICB, CCB)	After ICV and every IPC	< CRDL	1. Terminate analysis 2. Identify and document the problem 3. Recalibrate, verify and reanalyze all associated samples
CRDL Verification Standard	After initial IPC/CCB	$\pm 20\%$ from expected concentration	1. Reprep and reanalyze standard 2. Recalibrate and verify

<sup>3</sup> The ICAL low standard must be between the CRDL and 2X CRDL.

<sup>5</sup> Report the retention time window for each analyte. Determine retention time windows as  $\pm 10\%$  of the mean retention time for each analyte in the calibration standards.

Table 3. Summary of Internal Quality Control Procedures for Inorganic Anions by EPA Method 300.0

{PRIVATE }QC Element	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank (LRB)	One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum)	< CRDL	1. If lowest sample concentration is more than 10X the blank conc., no action 2. If samples are non-detected, no action 3. If detected sample concentrations are less than 10X blank conc., all associated samples must be prepared again with another method blank and reanalyzed
Duplicate Sample (DUP)	One per batch or SDG (1 per 20 samples minimum)	RPD <20% for samples >5X CRDL; $\pm$ CRDL for samples <5X CRDL	1. Flag associated data with an "*"
Laboratory Fortified Matrix (LFM)	One per batch or SDG (1 per 20 samples minimum)	$\pm$ 25% from expected value <sup>b</sup>	1. Flag associated data with an "N"
Laboratory Fortified Blank (LFB)	One per batch or SDG (1 per 20 samples minimum)	$\pm$ 10% from expected concentration	1. Terminate analysis 2. Identify and document the problem 3. Reanalyze all associated samples

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

<sup>b</sup> An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of 4. In such an event, the data shall be reported unflagged.

Dilute and reanalyze samples with concentrations exceeding the range of the calibration curve. Results for

such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

If resolution is inadequate or analyte identification is questionable, fortify the sample with an appropriate amount of standard and reanalyze.



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## Method Summary Information

<b>Method Number:</b>	300.0	<b>Media:</b>	WATER	
<b>Revision:</b>	Revision 2.1, August 1993			
<b>Method Source:</b>	U.S. EPA National Exposure Research Laboratory (NERL) [formerly EMSL]			
<b>Subcategory:</b>	INORGANIC			
<b>Official Name:</b>	Determination of Inorganic Anions by Ion Chromatography			
<b>Descriptive Name</b>	Inorganic Anions by Ion Chromatography			
<b>Source Info:</b>	U.S.EPA National Exposure Research Laboratory (NERL) Microbiological and Chemical Exposure Assessment Research Division (MCEARD) [formerly the Environmental Monitoring Systems Laboratory (EMSL), Cincinnati, OH] 26 West Martin Luther King Drive Cincinnati, Ohio 45268-0001 Fax: 513-569-7757 email: <a href="mailto:DWmethods.help@epa.gov">DWmethods.help@epa.gov</a>			

[Analytes in this method](#)

**Citation:** Methods for the Determination of Inorganic Substances in Environmental Samples (EPA/600/R-93/100)

 [Download the complete method in PDF format](#) [Byte file](#)

**Brief Method Summary:** A small volume of sample, typically 50-100 uL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

**Scope And Application:** Part A of the test method covers the determination of common inorganic anions in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction), leachates (when no acetic acid is used). Part B of the test method covers the determination of bromate, chlorate, and chlorite in drinking and reagent waters.

**Applicable Conc Range:** DL - \* (\* Upper detection limit is defined as the highest calibration point, as determined by analyst.)

**Interferences:** (1) Coeluting species (e.g., low-molecular-weight organic acids). (2) High concentration of anions can effect resolution of peaks and elution times. (3) Fluoride is especially sensitive to coeluting species, and "water dip" (corresponding to the elution of water) at low concentrations.

QC Requirements:

Calibration Blank (CB), Quality Control Sample (QCS), Performance Evaluation Sample (PE), Instrument Performance Check Solution (IPC), Laboratory Duplicate (LD), Field Duplicate (FD), Laboratory Fortified Matrix (LFM), Laboratory Fortified Blank (LFB), Laboratory Reagent Blank (LRB), Linear Calibration Range (LCR)

Sample Handling:

Collect enough volume to ensure a representative sample and to allow for replicates. Either glass or plastic bottles may be used.

For Part A Analytes: No preservation is required for bromide, chloride, or fluoride. Refrigerate samples at 4 degrees C for nitrate-N, nitrite-N, orthophosphate-P, and sulfate. Samples being tested for nitrate/nitrite should be adjusted to pH < 2 with concentrated H<sub>2</sub>SO<sub>4</sub> and refrigerated at 4 degrees C until analysis. Analyze samples being tested for bromide, chloride, fluoride, nitrate/nitrite, and sulfate within 28 days. Analyze samples being tested for nitrate-N, nitrite-N, and orthophosphate-P within 48 hours.

For Part B Analytes: Samples analyzed for bromate and chlorate may be held for 28 days without preservation. Chlorite should be analyzed for immediately (within 10 minutes). However, if the sample cannot be analyzed immediately, it may be preserved for up to 14 days if treated with ethylenediamine (ClO<sub>2</sub> should be removed prior to this step) and chilled to 4°C.

Max Holding Time:

Part A: 48 Hours (NO<sub>2</sub>-N, NO<sub>3</sub>-N, orthophosphate-P) 28 days (others)  
Part B: Bromate and Chlorate (28 days) and chlorite (14 days with preservation -- otherwise analyze immediately).

Relative Cost:

\$51 to \$200  
4680







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## List of Analytes

Method <input type="text" value="300.0"/> provides analyses for <input type="text" value="10"/> analyte(s), listed below. (Note: Accuracy and precision notes may be included below the list of analytes)					
Analyte	Detection level	Accuracy	Percent False +/-	Precision	Instrumentation
<b>Bromate</b> 15541-45-4	.02 mg/L	N/A	N/A	N/A	Ion Chromatography
<b>Bromide</b> 24959-67-9	.01 mg/L	99 % Rec (SL)	2	RSD (SL)	Ion Chromatography
<b>Chlorate</b> 14866-68-3	.003 mg/L	110 % Rec (SL)	10	RSD (SL)	Ion Chromatography
<b>Chloride</b> 16887-00-6	.02 mg/L	96 % Rec (SL)	2	RSD (SL)	Ion Chromatography
<b>Chlorite</b> 14998-27-7	.01 mg/L	94 % Rec (SL)	20	mg/L	Ion Chromatography
<b>Fluoride</b> 16984-48-8	.01 mg/L	91 % Rec (SL)	.05	mg/L	Ion Chromatography
<b>Nitrate</b> 	.002 mg/L	103 % Rec (SL)	3	RSD (SL)	Ion Chromatography

14797-55-8	Spiking level: 10 mg/L		
Nitrite	.004 mg/L	97 % Rec (SL)	2 RSD (SL)
	14797-65-0	Spiking level: 10 mg/L	
Phosphate	.003 mg/L	99 % Rec (SL)	2 RSD (SL)
	14265-44-2	Spiking level: 10 mg/L	

Analyte	Detection level	Accuracy	Percent False + / -	Precision	Instrumentation
Sulfate	.02 mg/L	99 % Rec (SL)	2 RSD (SL)	2 RSD (SL)	Ion Chromatography
	14808-79-8	Spiking level: 20 mg/L			

Comments on precision and accuracy fields:      Comments on detection level field:

Precision and accuracy were obtained from a single operator study, analyzing 7 replicate reagent water samples. Additional precision and accuracy data, including data from

Not explicitly described



CARBONATE, BICARBONATE, and TOTAL ALKALINITY  
Standard Methods 2320 (Titration Method)

Table 1. Summary of Contract Required Detection Limits, Holding Times, and Preservation for Alkalinity

Analytical Parameter	Contract Required Detection Limit (CRDL)	Technical and Contract Holding Times	Preservation
Low-Level Alkalinity:	2 mg/L	Technical: 14 Days from collection; Contract: 12 Days from receipt at laboratory	Cool to 4EC $\pm$ 2EC*
High-Level Alkalinity:	20 mg/L		

\* Samples must be unfiltered

**Data Calculations and Reporting Units:**

Calculate the sample results according to Section 5 of Standard Methods 2320.

Report sample results in concentration units of milligram per liter (mg/L) as calcium carbonate ( $\text{CaCO}_3$ ). Report  $\text{CaCO}_3$  concentrations that are less than 10 mg/L to 2 significant figures, and  $\text{CaCO}_3$  concentrations that are greater than or equal to 10 mg/L to 3 significant figures.

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

Table 2. Summary of Internal Quality Control Procedures for Carbonate, Bicarbonate and Total Alkalinity  
by SM 2320

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum)	< CRDL	1. If lowest sample concentration is more than 10X the blank conc., no action 2. If samples are non-detected, no action 3. If detected sample concentrations are less than 10X blank conc., all associated samples must be prepared again with another method blank and reanalyzed
Duplicate Sample (DUP)	One per batch or SDG (1 per 20 samples minimum)	RPD <20% for samples >20 mg/L; $\pm$ CRDL for samples <20 mg/L	1. Flag associated data with an "**"
Mineral Reference Samples	One set (at two concentration levels, one low, one high) per batch or SDG	$\pm$ 15% from expected concentration	1. Terminate analysis 2. Identify and document the problem 3. Reanalyze all associated samples

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

Standardize pH meter daily, using at least 2 buffers.

Standardize titrant whenever prepared or monthly, whichever comes first.

Do not use titrant volumes greater than 50 mL. Reanalyze any sample requiring more than 50 mL of titrant, selecting a smaller aliquot of sample, or performing the titration with a higher normality standard acid.





## METHOD 3050B

### ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

#### 1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detection limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

<u>FLAA/ICP-AES</u>		<u>GFAA/ICP-MS</u>
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		
Vanadium		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

#### 2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid ( $\text{HNO}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first



with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

### 3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

### 4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain  $30^{\circ}\text{C} \pm 4^{\circ}\text{C}$ .

4.4 Temperature measurement device capable of measuring to at least  $125^{\circ}\text{C}$  with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of  $90\text{--}95^{\circ}\text{C}$ . (e.g., hot plate, block digester, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

### 5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated),  $\text{HNO}_3$ . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated),  $\text{HCl}$ . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%),  $\text{H}_2\text{O}_2$ . Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

## 7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1  $\text{HNO}_3$ , mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to  $95^\circ\text{C} \pm 5^\circ\text{C}$  and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated  $\text{HNO}_3$ , replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by  $\text{HNO}_3$ , repeat this step (addition of 5 mL of conc.  $\text{HNO}_3$ ) over and over until no brown fumes are given off by the sample indicating the complete reaction with  $\text{HNO}_3$ . Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at  $95^\circ\text{C} \pm 5^\circ\text{C}$  without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO<sub>3</sub>, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO<sub>3</sub>, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO<sub>3</sub>, repeat this step (addition of 5 mL concentrated HNO<sub>3</sub>) until no brown fumes are given off by the sample indicating the complete reaction with HNO<sub>3</sub>. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H<sub>2</sub>O<sub>2</sub>. Care must be taken to ensure that losses do not occur due to excessive vigorous effervescence. Go to Section 7.2.3.

7.2.2 Continue to add 30% H<sub>2</sub>O<sub>2</sub> in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H<sub>2</sub>O<sub>2</sub>.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO<sub>3</sub>. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

**NOTE:** Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H<sub>2</sub>O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

**NOTE:** Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO<sub>3</sub> and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

**NOTE:** High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

## 7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

## 8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

## 9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

## 10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
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TABLE 1  
STANDARD RECOVERY (%) COMPARISON FOR  
METHODS 3050A AND 3050B<sup>a</sup>

Analyte	METHOD 3050A <sup>a</sup>	METHOD 3050B w/option <sup>a</sup>
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

<sup>a</sup> All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2  
PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Percent Recovery <sup>a,c</sup>							
	<u>Sample 4435</u>		<u>Sample 4766</u>		<u>Sample HJ</u>		<u>Average</u>	
	<u>3050A</u>	<u>3050B</u>	<u>3050A</u>	<u>3050B</u>	<u>3050A</u>	<u>3050B</u>	<u>3050A</u>	<u>3050B</u>
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.



Table 3  
Results of Analysis of Nist Standard Reference Material 2704  
"River Sediment" Using Method 3050B ( $\mu\text{g/g} \pm \text{SD}$ )

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion ( $\mu\text{g/g} \pm 95\% \text{ CI}$ )
Cu	101 $\pm$ 7	89 $\pm$ 1	98 $\pm$ 1.4	100 $\pm$ 2	98.6 $\pm$ 5.0
Pb	160 $\pm$ 2	145 $\pm$ 6	145 $\pm$ 7	146 $\pm$ 1	161 $\pm$ 17
Zn	427 $\pm$ 2	411 $\pm$ 3	405 $\pm$ 14	427 $\pm$ 5	438 $\pm$ 12
Cd	NA	3.5 $\pm$ 0.66	3.7 $\pm$ 0.9	NA	3.45 $\pm$ 0.22
Cr	82 $\pm$ 3	79 $\pm$ 2	85 $\pm$ 4	89 $\pm$ 1	135 $\pm$ 5
Ni	42 $\pm$ 1	36 $\pm$ 1	38 $\pm$ 4	44 $\pm$ 2	44.1 $\pm$ 3.0

NA - Not Available

Table 4  
Results of Analysis of NIST Standard Reference Material 2710  
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B  
( $\mu\text{g/g} \pm \text{SD}$ )

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion ( $\mu\text{g/g} \pm 95\% \text{ CI}$ )
Cu	2640 $\pm$ 60	2790 $\pm$ 41	2480 $\pm$ 33	2910 $\pm$ 59	2700	2950 $\pm$ 130
Pb	5640 $\pm$ 117	5430 $\pm$ 72	5170 $\pm$ 34	5720 $\pm$ 280	5100	5532 $\pm$ 80
Zn	6410 $\pm$ 74	5810 $\pm$ 34	6130 $\pm$ 27	6230 $\pm$ 115	5900	6952 $\pm$ 91
Cd	NA	20.3 $\pm$ 1.4	20.2 $\pm$ 0.4	NA	20	21.8 $\pm$ 0.2
Cr	20 $\pm$ 1.6	19 $\pm$ 2	18 $\pm$ 2.4	23 $\pm$ 0.5	19	39*
Ni	7.8 $\pm$ 0.29	10 $\pm$ 1	9.1 $\pm$ 1.1	7 $\pm$ 0.44	10.1	14.3 $\pm$ 1.0

NA - Not Available \* Non-certified values, for information only.

CD-ROM

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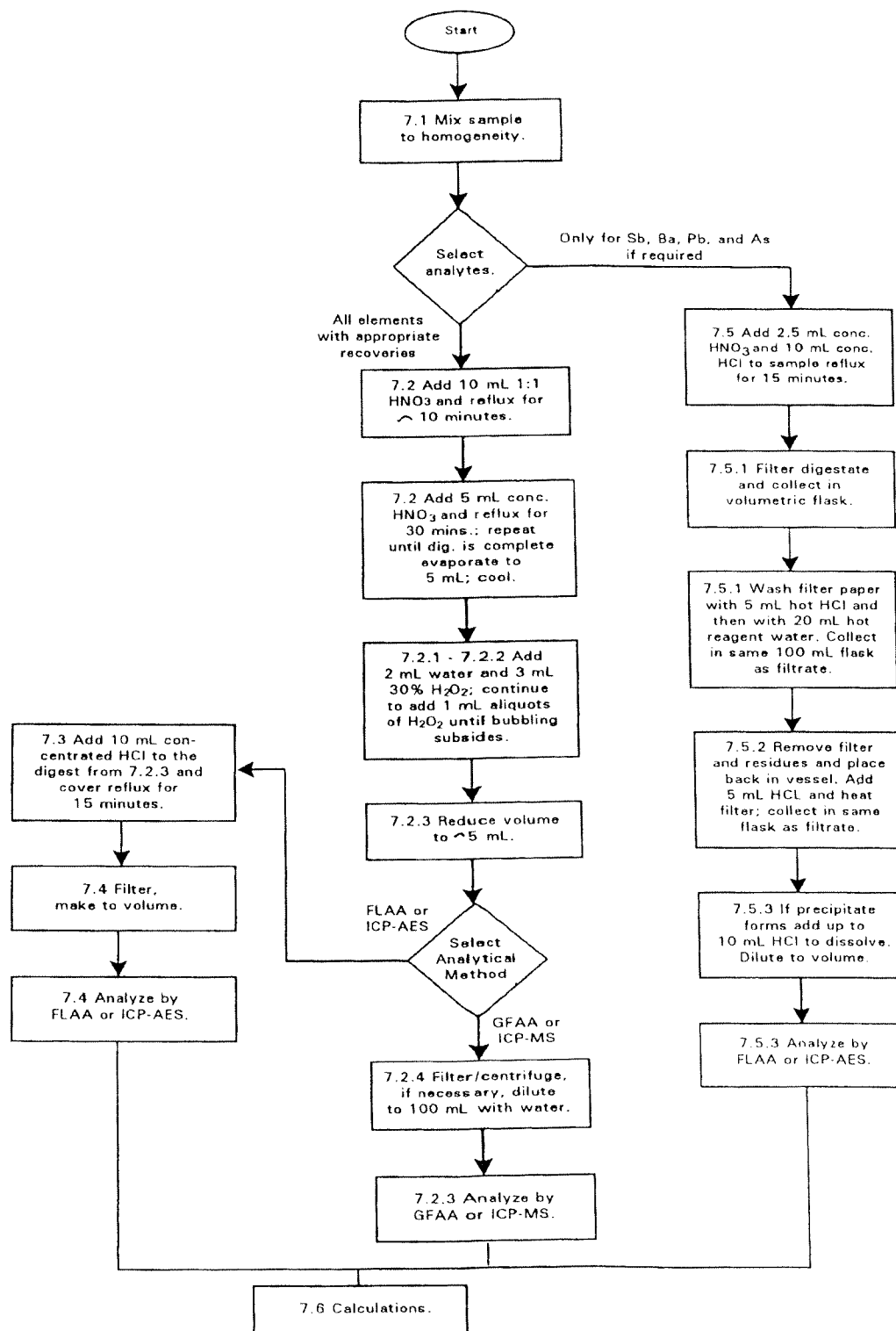
Table 5  
Results of Analysis of NIST Standard Reference Material 2711  
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B  
( $\mu\text{g/g} \pm \text{SD}$ )

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion ( $\mu\text{g/g} \pm 95\% \text{ CI}$ )
Cu	107 $\pm$ 4.6	98 $\pm$ 5	98 $\pm$ 3.8	111 $\pm$ 6.4	100	114 $\pm$ 2
Pb	1240 $\pm$ 68	1130 $\pm$ 20	1120 $\pm$ 29	1240 $\pm$ 38	1100	1162 $\pm$ 31
Zn	330 $\pm$ 17	312 $\pm$ 2	307 $\pm$ 12	340 $\pm$ 13	310	350.4 $\pm$ 4.8
Cd	NA	39.6 $\pm$ 3.9	40.9 $\pm$ 1.9	NA	40	41.7 $\pm$ 0.25
Cr	22 $\pm$ 0.35	21 $\pm$ 1	15 $\pm$ 1.1	23 $\pm$ 0.9	20	47*
Ni	15 $\pm$ 0.2	17 $\pm$ 2	15 $\pm$ 1.6	16 $\pm$ 0.4	16	20.6 $\pm$ 1.1

NA - Not Available

\* Non-certified values, for information only.

METHOD 3050B  
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS





## METHOD 5035

### CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

#### 1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

### 3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

### 4.0 APPARATUS AND MATERIALS

#### 4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

## 4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocab 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocab 4000 but performs adequately when Vocab 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carboxpack/Carboxieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If



the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

#### 4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-μL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-μL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

#### 4.4 Miscellaneous

##### 4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

#### 4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

### 5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH<sub>3</sub>OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), H(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, NaHSO<sub>4</sub> - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

### 6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

#### 6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of  $\leq 2$ .

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the